United States Patent Application for:

Selectable Ion Concentrations with Electrolytic Ion Exchange

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Background

Embodiments of the invention relate to ion exchange processes and apparatus.

Ion exchange cells are used to remove or replace dissolved solids or ions in solutions. For example, ion exchange membranes and beads are used to deionize water to produce high purity drinking water by removing contaminant and other dissolved solids from a municipal wastewater streams. Ion exchange is also used for the selective substitution of ions in the treatment of industrial wastewater. In another example, tap water is softened by replacing hard divalent ions in tap water, such as calcium, with soft monovalent ions, such as sodium or potassium. Typically, ion exchange efficiency is measured by determining the total dissolved solids (TDS) content of a treated and untreated solutions and reported as a percentage reduction (%R).

Electrolytic assisted ion exchange improves ion extraction efficiency and provides easier regeneration of the ion exchange material in the cell. In such a system, an electric field is applied across a water-splitting ion exchange membrane, as described in commonly assigned U.S. Patent No. 5,788,826 to Nyberg, which is incorporated herein by reference in its entirety. The water splitting membrane typically comprises a strong-acid cation exchange surface or layer (sulfonate groups; $-SO_3M$) and a strong-base anion exchange surface or layer (quaternary ammonium groups; $-NR_3A$). The membrane is positioned between electrodes so that its cation exchange surface faces the first electrode and its anion exchange surface faces the second electrode. During a deionization process cycle, a solution stream is passed through the cell while a predetermined voltage level is applied to the electrodes to generate an electric field normal to the surfaces of the water-splitting membrane. The electric field irreversibly dissociates water to split it into its component ions H^+ and OH^- that migrate through the ion exchange layers in the direction of the electrode having an opposite polarity (e.g., H^+ migrates toward the negative electrode). The electric field assists the transport of the dissolved solid ions generated by the water-splitting reaction in a direction perpendicular to the membrane to provide a short pathway through the membrane. Thus, during deionization, the electric field is set at a single level that is sufficiently high to dissociate the water and effectively transport and remove a large majority of dissolved solids from the solution. The predetermined fixed field strength is generated by applying a single high DC voltage to the electrodes that maximizes ion

extraction. Electrolytic ion exchange advantageously provides a uniform electric field in the cell that better utilizes the entire surface area of the membrane and that increases ion exchange efficiency to be able to remove 90% or more of the dissolved solids.

5   Electrolytic assisted ion exchange systems also allow electrical regeneration of the membranes, which is advantageous over conventional chemical regeneration processes. Conventional cation exchange layers are commonly regenerated using acidic solutions, such as sulfuric acid; and anion exchange layers are regenerated using basic solutions, such as sodium hydroxide. Regeneration is

10   concluded with a rinsing step that removes entrapped regenerant solution. These chemical processes require large amounts of regenerating chemicals and/or water, and the cell has to be periodically shut down to allow the regeneration process. However, in electrolytic assisted ion exchange processes, the water-splitting membrane is regenerated by simply reversing the polarity of the voltage applied to electrodes to

15   generate an inverted electric field that electrically regenerates the membranes by disgorging exchanged ions from the membrane. The reverse polarity voltage is also applied at a single voltage level that maximizes ion expulsion and/or rejection efficiency from the water splitting membrane during the regeneration cycle.

20   However, conventional electrolytic assisted ion exchange systems have several limitations. One limitation is that the TDS removal fraction can vary with influent solution quality and cell operating conditions. For example, a change in the flow rate or pressure of the influent solution can result in different fractions of dissolved solids being removed. The total dissolved solids content of the effluent solution also varies due to

25   the TDS content of the influent solution changing with time, for example, the TDS of sewage changes drastically with heavy rains. As a result, an electrolytic cell that provides a 90% TDS reduction will generate a treated effluent solution having a TDS of 15 ppm from an influent solution having a TDS of 150 ppm, but when the influent solution contains 1500 ppm TDS, the treated effluent solution will have a TDS of 150

30   ppm. Such variations in the output TDS content are undesirable. Conventional electrolytic ion exchange cells also often exhibit a gradual increase in TDS content in the effluent solution, as the working ion exchange capacity of the membrane is consumed during deionization, which further increases the variability in effluent solution TDS content. The slow increase of ion concentration during batch deionization

35   processes can cause the premature end of the deionization cycle, well before the capacity of the membrane is truly exhausted, increasing capital and operating costs for

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the cell. Thus, the output TDS content can vary significantly with influent TDS content and over time with conventional systems.

Furthermore, conventional electrolytic ion exchange systems also do not allow control of the ion concentration. While maximizing extraction of ions from a solution stream is desirable to purify water and de-ionized water in industrial applications, in some applications, it is desirable to maintain a predefined level of dissolved solids in the solution stream. For example, in drinking and cooking water applications, some dissolved solids are desirable so the water tastes better and does not taste synthetic. In other industrial water applications, it is also desirable to reduce the level of a particular ion in a wastewater stream, for example nitrate or arsenic ions, to meet an environmental standard. A particular ion level in a chemical solution can also be needed to provide precise control of the composition of the solution for industrial processes, for example, in cement manufacture and in electroplating solutions.

Thus, it is desirable to be able to treat influent solutions to provide uniform and consistent ion concentrations in the effluent solution, even if the quality or TDS of the influent solution varies over the treatment process. There is also a need for a water treatment system that can use electrical power for regeneration of ion exchange materials that uses electrical power rather than chemicals for regeneration to reduce or eliminate the inconvenience and environmental hazards associated with regenerant chemicals, and reduce rinse water volumes during cleaning cycles. It is also desirable to be able to treat influent solutions to maintain a predetermined or set level of dissolved solids in the treated solution.

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SUMMARY

An apparatus to treat an influent solution comprising ions to obtain a selectable ion concentration in a resultant effluent solution. The apparatus comprises an electrochemical cell comprising a housing comprising first and second electrodes. A water-splitting ion exchange membrane is between the first and second electrodes, the membrane comprising a cation exchange surface facing the first electrode and an anion exchange surface facing the second electrode. The housing also has an influent solution inlet and an effluent solution outlet with a solution channel that allows influent solution to flow past both the anion and cation exchange surfaces of the water-splitting ion exchange membrane to form the effluent solution. A variable voltage supply is capable of maintaining the first and second electrodes at a plurality of voltage levels during an ion exchange stage. The ion exchange stage can be, for example, a deionization or ion removal step, or a membrane regeneration or ion rejection step.

In one version, the apparatus includes an ion meter to measure an ion concentration of the influent solution, at least partially treated influent solution, or effluent solution, and generate an ion concentration signal. A controller receives the ion concentration signal from the ion meter, and sends a control signal to the variable voltage supply to adjust the voltage level applied to the first and second electrodes in response to the ion concentration signal to achieve a predefined ion concentration range in the effluent solution.

In another aspect, a method of treating an influent solution comprising ions to control the concentration of ions in an effluent solution, is provided. The method comprises flowing the influent solution past both anion and cation exchange surfaces of a water-splitting ion exchange membrane to form the effluent solution; maintaining a time averaged electric field across the cation and anion exchange surfaces of the water-splitting membrane; and varying the strength of the time averaged electric field to control the ion concentration of the effluent solution.

DRAWINGS

These features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims,
5   and accompanying drawings which illustrate exemplary features of the invention:

Figure 1 is a schematic sectional side view of an embodiment of the apparatus of the present invention illustrating an electrolytic ion exchange cell, power supply and control system;
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Figure 2 is a sectional view of sectional side view of another embodiment of the apparatus having an electrolytic ion exchange cell comprising a spiral membrane;

Figure 3 is a top view of the electrolytic ion exchange cell of Figure 2;
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Figure 4 is a graph showing a variable time averaged voltage for an ion removal step (a) and an ion rejection (b);

Figure 5 is a circuit diagram of a variable voltage supply comprising a
20   phase control voltage supply;

Figures 6a-c are graphs showing exemplary input AC voltage and DC output voltage waveforms produced by the phase control voltage supply of Figure 5;

25   Figure 7a is block diagram of a switching voltage supply with pulse width modulation;

Figure 7b and c are graphs showing an input AC voltage signal and an output duty cycle modulated DC voltage generated by the voltage supply of Figure 7a;
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Figure 8 is a circuit diagram of a switching DC voltage supply 90;

Figure 9 is a schematic sectional view of an embodiment the apparatus that uses current and voltage measurements to control the voltage applied to the
35   electrodes of a cell;

Figure 10a is an embodiment of the present invention comprising two cells connected in parallel;

5   Figure 10b is an embodiment comprising two cells connected in series;

Figure 10c is an embodiment comprising two cells connected in series, and employing constant voltage and a variable voltage power supplies; and

10   Figure 11 is a graph that shows the comparative conductivity levels obtained for effluent solutions treated with a constant voltage level (constant voltage) or a variable voltage level (variable voltage).

DESCRIPTION

An embodiment of the present apparatus **20** is capable of treating an influent solution comprising ions to extract, replace, or add ions to generate an effluent solution having desired ion concentrations. Exemplary embodiments of the ion controlling apparatus **20** are provided to illustrate the invention and should not be used to limit the scope of the invention, and alternative cell arrangements and configurations as would be apparent to those of ordinary skill in the art are within the scope of the invention. Generally, the apparatus **20** comprises an electrochemical cell **22** comprising a housing **25** that is an enclosed leak proof structure having at least one influent solution inlet **30** and at least one effluent solution outlet **35**, as shown in Figure 1. A suitable housing **25** typically comprises a plate and frame construction fabricated from metal or plastic. While one or more outlets **35** can be provided, the effluent solution from the housing **25** preferably comprises a single effluent solution stream that is formed before or after the outlet **35**, for example in an exhaust manifold that combines the different solution streams. Optionally, a pump **38**, such as for example, a peristaltic pump or water pressure in combination with a flow control device can be used to flow influent solution into the inlet **30** of the housing **25**.

The housing **25** has first and second electrodes **40, 45** therein. One or more of the electrodes **40, 45** can form a portion of the housing **25**, for example an electrically conducting wall of the housing as shown in Figure 3 or can be a discrete structure such as a free standing plate inside the housing (as shown) in Figure 1. Typically, the electrodes **40, 45** have conducting surfaces that face one another. The anode and cathode electrodes **40, 45** are fabricated from electrically conductive materials, such as metals which are preferably resistant to corrosion in the low or high pH chemical environments created during positive and negative polarization of the electrodes during operation of the cell **22**. Suitable electrodes can be fabricated from corrosion-resistant materials such as titanium or niobium, and can have an outer coating of a noble metal, such as platinum. The shape of the electrodes **40, 45** depends upon the design of the electrochemical cell **22** and the conductivity of the influent solution **70** flowing through the cell **22**. A suitable electrode is a flat plate that provides a uniform voltage across its surfaces, and that can have openings to allow influent solution to pass therethrough. In another arrangement, the electrodes **40,45** are shaped as spirals, discs, or even conical shapes.

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A water-splitting ion exchange membrane **100** is between the first and second electrodes **40, 45**, the membrane **100** comprising an anion exchange surface **46** facing the first electrode **40**, and a cation exchange surface **48** facing the second electrode **45** as shown in Figure 1, or vice versa as shown in Figure 2. The water-splitting membrane **100** can comprise abutting anion and cation layers **49, 51**, respectively, contained in an open frame **47** positioned between the electrodes **40, 45**, or can be arranged in a spiral configuration as shown in Figures 2 and 3. Suitable anion exchange layers **49** of water-splitting membrane **100** comprise one or more basic functional groups capable of exchanging anions such as $-NR_3A$, $-NR_2HA$, $-PR_3A$, $-SR_2A$, or C_5H_5NHA (pyridine), where R is an alkyl, aryl, or other organic group and A is an anion (*e.g.*, hydroxide, bicarbonate, chloride, or sulfate ion). The choice of anion exchange functional group also depends on the application. In water deionization, $-NR_3A$ is preferred for its ability to impart good membrane swelling, and thus provide low electrical resistances and high mass transport rates, over a wide range of pH. Weak base groups are preferred when particularly efficient regeneration is required. For example, $-NR_2HA$ will react with OH^- in a very favorable reaction to form $-NR_2$, H_2O, and expel A^-. Suitable cation exchange layers **51** can comprise one or more acidic functional groups capable of exchanging cations such as $-COOM$, $-SO_3M$, $-PO_3M_2$, and $-C_6H_4OM$, where M is a cation (*e.g.*, hydrogen, sodium, calcium, or copper ion). Cation exchange materials also include those comprising neutral groups or ligands that bind cations through coordinate rather than electrostatic or ionic bonds (for example pyridine, phosphine and sulfide groups), and groups comprising complexing or chelating groups (*e.g.*, those derived from aminophosphoric acid, aminocarboxylic acid, and hydroxamic acid). The choice of cation exchange functional group depends upon the application of the cell **22**. In water deionization for which the non-selective removal of ions is required, $-SO_3M$ groups are preferred for their ability to impart good membrane swelling, high mass transport rates, and low electrical resistances over a wide range of pH. For the selective removal of copper ion from a liquid containing other ions, for example sodium ion, ion exchange groups such as $-COOM$ or a chelating group such as aminocarboxylic acid are preferred. These weak acid groups offer the additional benefit of particularly efficient regeneration due to the strongly favorable reaction of $-(COO)_nM$ with H^+ to form $-COOH$ and expel M^{+n}, where M is a metal ion.

The water-splitting ion exchange membranes **100** can also comprise more than two anion and cation exchange layers **49, 51**. For example, the water-splitting membrane **100** can have two cation exchange layers and two anion exchange layers.

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Each two cation or anion exchange layer differs in ion exchange capacities or ion exchange functional groups. For example, a first inner cation exchange layer of water-splitting membrane **100** may comprise substantially $-SO_3$ groups and an outer cation layer can comprise -COOH groups; while the inner anion exchange layer comprises -

5   NR_3 groups and the outer anion layer comprises $-NR_2H$ groups. The anion and cation exchange layers can also be porous to hold solution, for example, an open cell foam or other structure, to provide faster solution transport through the water-splitting ion exchange membrane.

10   A solution channel **52** in the housing **25** allows influent solution **70** from the inlet **30** to flow past both the anion and cation exchange surfaces **46, 48** of the water-splitting ion exchange membrane **100** to form the effluent solution **80** at the outlet **35**. The flow path of solution channel **52** can be defined by the housing **25** and the structures in the housing **25**. For example, the channel **52** can be formed between the

15   surfaces of the water-splitting membranes **100**, the electrodes **40, 45**, and the sidewalls **54** of the housing **25**, as shown in Figure 1. The channel **52** can also be a tubular walled structure in the housing (not shown). The solution channel **52** extends from the inlet **30** to outlet **35** where it outputs treated effluent solution **80**.

20   An alternative embodiment of the electrochemical cell **22** comprises a first electrode **40** that forms an outer electrode structure and a second electrode **45** that forms a central electrode structure, as shown in Figure 2. The water-splitting membrane **100** comprises a plurality of anion and cation exchange layers **49, 51** that are positioned between the two electrodes **40, 45**. The membrane layers **49, 51** are

25   arranged in the housing **25** so that the cation exchange surfaces **48** of the membranes face the first electrode **40**, and the anion exchange surfaces **46** of the membranes face the second electrode **45**. The membranes layers **49, 51** form a spiral wrapped configuration with a spacer **43** which separates the cation surfaces **48** from the anion surfaces **46** and provides a solution channel **52**, as shown in Figure 3. Any number of

30   membranes **100** may be wrapped in parallel in this way to provide the desired pressure drop through the cell **22**. For example, three membranes **100** can be spiral wrapped in a parallel arrangement. Spacers **43** can also be positioned within the solution channel **52**. The spacers **43** can be, for example, layers of plastic netting material suspended form the sidewalls **54** of the cell. The spacers **43** can be used to separate the water-

35   splitting membranes **100**, provide more uniform flow, or create turbulence in the solution channel **52** to provide higher ion transport rates. If two or more water-splitting

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membranes **100** are in direct contact, excess current may flow through this low resistance path, overheating the membranes **100** and bypassing the solution (thereby reducing cell performance). The spacers **43** can have openings sized 10 μm or higher in diameter.

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The method of operation of the electrochemical cell **22** will be illustrated for the treatment of an influent solution comprising sodium chloride and for treatment of an influent solution comprising copper sulfate, in the cell **22** shown in Figures 2 and 3. Although operation of a cell **22** is illustrated with respect to these two selected

10   examples, it should be understood that the cell **22** and apparatus **20** can be used for many other applications, and should not be limited to the examples provided herein. In the first example, sodium chloride is removed and concentrated from the influent solution. The electrochemical cell **22**, as shown in Figure 2, comprises water-splitting membranes **100** having sulfonate cation exchange layers **51** and quaternary

15   ammonium anion exchange layers **49**. In the first step of the process, ion removal, a first electrode **40** facing the cation exchange layer **51** is positively charged (the anode), and the second electrode **45** is negatively charged (the cathode). At the interface between the cation and anion exchange layers **51, 49** of the water-splitting ion exchange membranes **100**, water in the solution stream is split into its component ions

20   H^+ and OH^-, and OH^- migrates through the cation exchange surfaces **48** toward the first (positive) electrode **40** while H^+ migrates through the anion exchange surfaces **46** toward the second (negative) electrode **45**. In this step, Na^+ diffuses and migrates through the cation exchange surfaces **48** in the direction of the negative electrode. The reactions occurring in the cation exchange layers **51** are:

25   (1) $P\text{-}SO_3H + Na^+ = P\text{-}SO_3Na + H^+$

            (2) $H^+ + OH^- = H_2O$
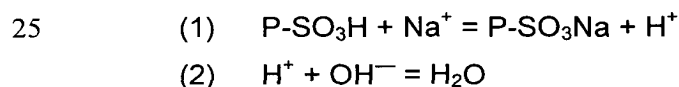
where "P" refers to the polymer or solid support to which the ion exchange group is attached. The OH^- produced by the water-splitting reaction and migrating through the cation exchange surfaces **48** reacts with H^+ to form water. The consumption of H^+

30   maintains the electric and concentration gradients which promote the rate of removal of Na^+ from solution.

Within the anion exchange layer **49**, Cl^- diffuses and migrates through the anion exchange layer **49** in the direction of the positive electrode. The reactions

35   occurring in the anion exchange layers **49** are:

            (3) $P\text{-}NR_3OH + Cl^- = P\text{-}NR_3Cl + OH^-$

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(4) $H^+ + OH^- = H_2O$
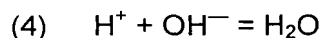
Analogous to the situation in the cation exchange layer **51**, the H^+ produced by the water-splitting reaction reacts with OH^- to promote the rate of removal of Cl^- from solution.

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     While the ion removal step can be performed without voltage (or current), ion removal rates are substantially slower due to the absence of the migration and chemical neutralization effects described above. Without voltage the irreversible water-splitting reaction does not occur, and thus neutralization reactions (2) and (4) cannot

10   take place. Ion removal rates are then governed exclusively by the diffusion rates of Na^+, H^+, Cl^-, and OH^- through the cation and anion exchange layers **51, 49**.

     After the ion exchange groups within the water-splitting membrane's cation and anion exchange layers **51, 49** are fully occupied by Na^+ and Cl^- ions, respectively,

15   a regeneration process step is required to return the water-splitting ion exchange membranes **100** to their original chemical form prior to reactions (1) to (4). In this step, a solution stream **70** is introduced into the cell **22**, as for example, the same sodium chloride solution treated in the first step, and the polarity of the electrodes is reversed so that the first electrode **40** is now the negative electrode and the second electrode **45**

20   is the positive electrode. In this step, H^+ produced by the water-splitting reaction moves through the cation exchange layer **51** in the direction of the negative electrode causing reaction (5):

(5) $P\text{-}SO_3Na + H^+ = P\text{-}SO_3H + Na^+$

Similarly, OH^- produced in the water-splitting reaction moves through the anion

25   exchange layer **49** in the direction of the positive electrode, causing reaction (6) to occur:

(6) $P\text{-}NR_3Cl + OH^- = P\text{-}NR_3OH + Cl^-$
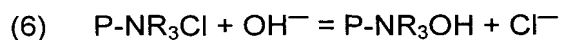
The Na^+ and Cl^- replaced by H^+ and OH^- in the cation and anion exchange layers **51, 49** combine to form NaCl in the effluent solution stream **80**. By controlling the solution

30   flow rate during this regeneration step, a concentration of NaCl substantially higher than was present in the incoming solution stream **70** during the ion removal step can be produced. If ion removal in reactions (1) to (4) was intended to deionize a solution stream, then the NaCl concentrate formed during reactions (5) and (6) is discarded. If the purpose of NaCl removal in this apparatus was to isolate this salt, then the NaCl

35   concentrate is saved for further processing.

The operation of this exemplary cell **22** will be described in the context of the removal and subsequent concentration of $CuSO_4$ from a solution. Any suitable ion exchange materials can be used in the cation and anion exchange layers **51, 49** of the water-splitting membranes **100**. For example, the cation exchange layers **51** may

5   comprise P-COOH groups, and the anion exchange layers **49** may comprise $P-NR_2H$ groups. During ion removal, OH^- produced in the water-splitting reaction again moves through the cation exchange layers **51** toward the positive electrode, and reactions (7) and (8) occur within the cation exchange layers **51**:

$$(7) \quad P\text{-}COOH + OH^- = P\text{-}COO^- + H_2O$$

10      $$(8) \quad 2\ P\text{-}COO^- + Cu^{+2} = (P\text{-}COO)_2Cu$$

Cu^{+2} cannot replace H^+ in P-COOH directly due to unfavorable thermodynamics, and thus reaction (7) is required to remove H^+ from P-COOH, forming $P\text{-}COO^-$ which readily reacts with Cu^{+2}.
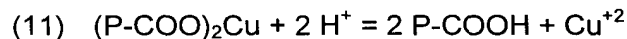
15   In the anion exchange layers **49**, H^+ produced in the water-splitting reaction moves through the anion exchange layers **49** toward the negative electrode, causing reactions (9) and (10) to occur:

$$(9) \quad P\text{-}NR_2 + H^+ = P\text{-}NR_2H^+$$

$$(10) \quad 2\ P\text{-}NR_2H^+ + SO_4^{-2} = (PNR_2H)_2SO_4$$
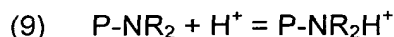
20   Reaction (9) forms an ionic group from the neutral $P\text{-}NR_2$, enabling the subsequent reaction with SO_4^{-2} in reaction (10).

When ion removal is complete, the cation and anion exchange layers **51, 49** are returned to their condition prior to ion removal by flowing the same or a different

25   solution through the cell **22** and reversing the polarity of the electrodes **40, 45**. H^+ produced in the water-splitting reaction now moves through the cation exchange layers **51**, resulting in reaction (11):

$$(11) \quad (P\text{-}COO)_2Cu + 2\ H^+ = 2\ P\text{-}COOH + Cu^{+2}$$

and OH^- produced in the water-splitting reaction moves through the anion exchange

30   layers **49**, resulting in reaction (12):

$$(12) \quad (P\text{-}NR_2H)_2SO_4 + 2\ OH^- = 2\ P\text{-}NR_2 + 2\ H_2O + SO_4^{-2}$$
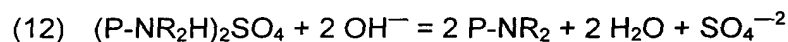
Both reactions (11) and (12) are thermodynamically favorable, allowing the concentration of $CuSO_4$ in the solution stream. In a subsequent step, the copper and/or sulfate may be recovered from the solution stream or discarded.

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The method of replacing ions in an ion exchange material illustrated in the two preceding examples may be described in general terms as follows. The water-splitting membranes **100** comprise ion exchange layers A and B, one a cation exchange layer **51** and the other an anion exchange layer **49**, which layers contain ions

5   I_{1A} and I_{1B}, respectively. An ion-containing solution electrically connects the electrodes **40, 45** and the water-splitting membranes **100**, and upon application of a sufficient voltage to the two electrodes **40, 45**, water at the interfacial region between ion exchange layers A and B is "split" into its component ions H^+ and OH^-. This phenomenon, referred to as the "water-splitting reaction," involves the spontaneous

10   dissociation of water into component ions H^+ and OH^- (dissociation occurs with or without the electric field), followed by the migration of these ions into ion exchange layers A and B under the influence of the electric field. H^+ migrates toward the negative electrode, and OH^- toward the positive electrode. As the H^+ and OH^- migrate into layers A and B, more water diffuses to the interfacial region to continue the water-splitting

15   reaction cycle. As H^+ and OH^- move through ion exchange layers A and B, they cause the replacement of ions I_{1A} and I_{1B} by ions I_{2A} and I_{2B} from the solution, respectively. This replacement of ions in ion exchange layers A and B may be either a direct replacement, for example H^+ for Na^+ on a $P-SO_3^-$ ion exchange group, or it may be an indirect replacement, for example as occurs when OH^- reacts in a first step with P-

20   COOH to form $P-COO^-$, followed by reaction to bind Cu^{+2}.

The apparatus **20** further comprises a variable voltage supply **50** to maintain the first and second electrodes **40, 45** at a plurality of voltage levels during an ion exchange stage. The voltage bias levels are selectable voltage levels that have

25   different magnitudes during the ion exchange stage. For example, the voltage levels can be time averaged voltage levels that are each a fixed constant voltage level or fixed pulsed voltage level, during a pre-specified time period that is a portion of the time period of an ion exchange stage, such as (i) a solution treatment step, for example, a deionization or ion removal step in which ions are removed from the influent solution **70**

30   to form the effluent solution **80**, or (ii) a membrane regeneration step or ion rejection step in which the membrane **100** is regenerated by expelling or replacing ions in the membrane, (ii) but not both. The ion removal step is a pass of the influent solution across the anion and cation surface **46, 48** of the water-splitting membrane **100** in the electrochemical cell **22** to change the ion concentration level in the influent solution **70**

35   by removing or replacing ions from the influent solution **70**. The ion rejection step is a regeneration cycle in which the water-splitting membrane **100** is regenerated by

expelling or rejecting ions in the membrane **100**. In each step, the time averaged voltage level is determined by averaging the magnitude of the voltage applied to the electrodes **40, 45** over a selected time period. The time period is a length of time in which the voltage has a peak absolute magnitude that remains substantially the same.

Figure 4 shows an exemplary embodiment of variable time averaged voltage levels for an ion removal step (graph (a)) and an ion rejection step (graph (b)). In this figure, the magnitude of the pulsed voltage is plotted over time to show different time cycles in each of which, the time-averaged voltage is maintained at one level. Graph (a) demonstrates a variable time averaged voltage applied to the electrode that has a first magnitude (V_1) that remains substantially the same over a first time period (T_1), a second first magnitude (V_2) that remains substantially the same over a second time period (T_2), a third magnitude (V_1) that remains substantially the same over a third time period (T_3), etc. Curve (b) shows a time averaged voltage having a reversed polarity with negative values of voltages (V_4) (V_5) (V_6) that are used during different time periods (T_4) (T_5) (T_6) of an ion rejection step. In each step, the time average voltage generates a time averaged electric field in the cell of different field strengths. The varying electric field has a field strength proportional to the different applied voltage levels. It should be noted that in the ion rejection step, the voltage can also remain substantially constant over the entire cycle, since the objective is only to expel ions from the membrane **100**.

In one version, the variable voltage supply **50** provides a time modulated or pulsed direct current (DC) voltage having a single polarity that remains either positive or negative, during an ion removal step, or during an ion rejection step. In contrast, a non-DC voltage such as an alternating current (AC) supply voltage, has a time-averaged AC voltage that would be approximately zero. Employing one polarity over the course of either an ion removal (deionization) or ion rejection (regeneration) step in the operation of the electrolytic ion exchange cell **22** allows ions in the influent solution **70** being treated to travel in a single direction toward or away from one of the electrodes **40, 45**, thereby providing a net mass transport of ions either into or out of the water-splitting membranes **100**. The magnitude of the average DC voltage is obtained by mathematically integrating the voltage over a time period and then dividing the integral by the time period. The polarity of the integration tells whether one is in ion removal or rejection mode, and the magnitude of this calculation is proportional to the electrical energy made available for ion removal or rejection. A reasonable estimate of

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this integrated value is obtained from the time-averaged measurement observed with a slow response DC voltmeter, for example, a voltmeter with a characteristic response time in the tens of seconds, such as 20-30 milliseconds. The voltage supply **50** can also includes a polarity switch **44** to switch polarity to the electrodes **40, 45**, for

5   example, to either momentarily add ions to solution to maintain a desired concentration in the solution in the cell **22** during the ion removal step, or to regenerate the membrane **100** in the cell **22** to prepare for a subsequent ion deionization step.

The variable voltage supply **50** can provide a variable DC voltage or
10   current by full-wave or half-wave rectification of an AC voltage. Such a voltage supply can be, for example, (i) a phase control voltage supply **50a**, or (ii) a switching voltage supply with pulse width modulation **50b**. These circuits and descriptions are only two examples of how to provide a variable time-modulated DC voltage, and other variable DC voltage supply circuits apparent to those of ordinary skill in the art can also be
15   employed. An embodiment of a phase control voltage supply **50a** using phase control thyristors (SCR) **81** is illustrated in Figure 5. The phase control voltage supply **50a** can provide linear or unregulated power. The voltage supply **50a** operates on conventional single phase AC power **82** (120 volts, 60 Hz) as shown in Figure 6a, inputted directly into back-to-back SCRs **81**that rectify the AC into DC. Besides rectification, the SCRs
20   **81** are also able to switch from non-conducting to conducting very rapidly. When an AC power source **82** is switched by an SCR **81**, the current is turned off every time the current drops to zero using the zero crossing trigger **91** that operates in combination with the trigger transistor **89**. Figure 6a shows an input AC cycle signal **72** of an SCR **81** that is triggered into conduction at a trigger point (t) that is about 2 milliseconds after
25   the AC cycle crosses zero voltage. At that point the SCR **81** turns on and remains on until the alternating wave crosses a zero voltage level. The back-to-back SCRs **81** function as full-wave rectifiers whose voltage output would be represented by the dotted line **76** in Figure 6b. Figure 6c shows the resulting waveform comprising a variable magnitude pulsed DC voltage **78**, which is then provided to the electrodes **40, 45** of the
30   cell **22**. In the phase control voltage supply **50a**, the SCRs **81** are turned on by an optotriac trigger SCR **83** and their timing determined by an RC circuit **84** comprising a 555 and 4066 control chips. The trigger occurs at a set time delay after the zero crossing **85** which is determined by varying the resistances **86** in RC timing circuit **84**. Continuous variation in the output voltage can be accomplished by using a
35   potentiometer. This circuit **50a** uses fixed resistors **86** to set six (or some other number) of discrete time delays to trigger the SCRs **81** at particular points in the

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alternating voltage phase thus setting five discrete output voltages at the output leads **87**, for example, 0 (off), 30, 100, 200, 300 volts.

In embodiment of a phase control voltage supply **50a** illustrated in Figure 5, there are a number of standard components, such as resistors, capacitors, diodes and transistors. Suitable values and part numbers that may be used for these components include: $C_1=C_2=250\mu F(250V)$, $C_3=0.01\mu F(50V)$, $C_4=0.1\mu F(25V)$, D_1 and D_2 are T6A1002, Q_1 and Q_2 are 2N6507 (SCRs), $R_2=100\Omega$, $R_4=1k\Omega$, $R_7=20k\Omega$, $R_8=22k\Omega$, $R_9=28k\Omega$, and $R_{14}=14k\Omega$. The above-listed values and components are only exemplary and different values or components can be used.

An alternative variable voltage supply **50** comprising a switching voltage supply with pulse width modulation **50b** is illustrated in the block diagram of Figure 7a. Given the input signal in Figure 7c, Figure 7b illustrates the output of the voltage supply **50b**. There is only one voltage level because the DC voltage or current power is controlled by varying the duty cycle, which is the ratio of on-time to off-time of the voltage. A version of the switching voltage supply **50b** that is a switching DC voltage supply **90**, is illustrated in Figure 8. In the voltage supply **90**, the AC power is rectified by unregulated DC rectifier and filter **93** before being transformed into a higher frequency and voltage. The modulator and inverter **94** uses a pulse width modulator **92** to regulate the voltage applied to the high frequency transformer **99**. The feedback loop compares the sampling feedback voltage **95** with a reference voltage **96** and controls the duty cycle of the primary transistor **98** to control the output voltage **97**.

The apparatus **20** can also include an ion sensor **59** to measure an ion concentration of the solution and generate a solution ion concentration signal. The ion sensor **59** can measure, for example, concentration, species type, or a ratio of concentrations of different ions. In one version, the ion sensor **59** is a conductivity sensor, which is useful to determine and control total dissolved solids (TDS) concentration in the treated effluent solution **80**. Alternatively, the ion sensor **59** can be a sensor specific to a particular ionic species, for example nitrate, arsenic or lead. The ion specific sensors can be for example, ISES (ion selective electrodes).

The location of the ion sensor **59** in the solution stream is selected depending on the nature of the ion concentration signal that is desired. The ion sensor can be used to (i) measure an ion concentration of the influent solution, at least partially

treated solution, or effluent solution, and (ii) generate an ion concentration signal, and In one version, the ion sensor **59** is placed in the at least partially treated solution after the influent solution **70** has passed across at least some of the cation and anion surfaces **48, 46** of the water-splitting membrane **100**. For example, the ion sensor **59**

5 can be placed near in the effluent solution stream beyond the effluent outlet **35**, as shown in Figure 2. In this version, the ion concentration signal represents the concentration of an ion, or ions, in the treated solution, and is used to adjust or regulate the ion extraction efficiency of the cell **22** to obtain a desired ion concentration in the cell **22**.

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A controller **53** receives the signal from the ion sensor **59** via a feedback circuit loop **57** and sends a control signal to the variable voltage supply **50** to control the voltage output to the electrodes **40, 45**. The controller **53** comprises electronic circuitry and program code to receive, evaluate, and send signals. For example, the controller

15 **53** can comprise (i) a programmable integrated circuit chip or a central processing unit (CPU), (ii) random access memory and stored memory, (iii) peripheral input and output devices such as keyboards and displays, and (iv) hardware interface boards comprising analog, digital input and output boards, and communication boards. The controller can also comprise program code instructions stored in the memory that is capable of

20 controlling and monitoring the electrochemical cell **22**, ion sensor **59**, and voltage supply **50**. The program code may be written in any conventional computer programming language. Suitable program code is entered into single or multiple files using a conventional text editor and stored or embodied in the memory. If the entered code text is in a high level language, the code is compiled, and the resultant compiler

25 code is then linked with an object code of pre-compiled library routines. To execute the linked, compiled object code, the user invokes the object code, causing the CPU to read and execute the code to perform the tasks identified in the program.

The controller **53** receives an ion concentration signal from the ion sensor

30 **59** and sends a control signal to the variable voltage supply **50** to adjust the voltage level provided by the voltage supply **50** to the electrodes **40, 45**. The signal sent by the controller **53** to the voltage supply **50** instructs the voltage supply **50** to adjust a time averaged voltage level applied to the electrodes **40, 45** in response to the signal from the ion sensor **59**. For example, the controller **53** can send a voltage control signal to

35 the voltage supply **50** to adjust the time averaged voltage level provided by the voltage supply **50** to achieve a predefined ion concentration range in the effluent solution **80**, as

described below. The controller **53** can also send a control signal to the variable voltage supply **50** to select the degree of power modulation or duty cycle of the time averaged voltage level.

5   A method of controlling ion or TDS concentration using the cell **22** shown in Figure 2, will be described using a measurement of the ionic conductivity of the treated effluent solution **80** by an ion sensor **59** comprising an ion conductivity sensor located just exterior to the outlet **35** of the cell **22**. Assuming an influent solution **70** having a conductivity of 1000 µS/cm (~500 ppm TDS) enters the cell **22** at inlet **30**, that
10   a desired conductivity of the treated solution 130 is 200 µS/cm (~100 ppm TDS), and that the cell **22** is initially powered at 100 V. As influent solution **70** passes through the cell **22**, cations are extracted by the ion exchange layers having surfaces **48** and anions are extracted by the ion exchange layers having surfaces **46**. The ion sensor **59** measures a lower ionic conductivity of the effluent solution **80** exiting the cell **22** via
15   outlet **35** that represents a reduced TDS concentration and generates a proportional ion concentration signal. The measured ion concentration signal is relayed to the controller **53**, which in turn sends a control signal to the variable voltage supply **50** by feedback loop **57**. If the measured conductivity of the effluent solution **80** is lower than the desired level of 200 µS/cm, then the controller **53** sends a control signal to the variable
20   power supply **50** to reduce the applied voltage. If the measured conductivity is greater than the desired level, then the controller **53** sends a control signal to the variable power supply **50** to increase the voltage. The controller **53** can contain a programmed microprocessor or program code to adjust the voltage to a proportional level based upon the difference between the target and measured ionic conductivity. If the
25   measured conductivity is nearer the target, the control signal instructs the variable voltage supply **50** to apply smaller voltage changes; and if measured conductivity is further from the target, the control signal instructs the voltage supply **50** to apply larger voltage changes. For example, if the measured ion concentration using the apparatus of Figure 1 is a specific ion, for example nitrate, then the controller **53** can send a
30   control signal to the variable power supply **50** containing instructions to adjust voltage to a predetermined level to decrease of increase the concentration of this specific ion.

          In another version, the ion sensor **59** is located in the influent solution **70** as far upstream as possible to obtain the earliest measurement of ion concentration in
35   the influent solution **70**, as for example, shown in Figure 1. It may also be located before the influent inlet **30** or interior to the cell **22** in a location that allows the desired

sensing of the ion content of the influent solution **70** before it is treated by the water-splitting membrane **100**. In this location, the ion sensor **59** generates an ion concentration signal that is indicative of the ion sensor **59**. The earlier the ion sensor **59** measurement can be determined in this embodiment, the more precisely can the ion

5   concentration of the treated solution be controlled.   The ion sensor **59** measures an ion concentration of the influent solution **70** and generates an influent ion concentration signal relating to the influent ion concentration. The controller **53** receives the influent ion concentration signal and sends a control signal to the variable voltage supply **50** to adjust the time-averaged voltage level in response to this signal. Feedback loop **57**,

10   controller **53** and variable voltage supply **50** adjust the voltage to cell **22** in response to the control signal to increase the voltage if the influent solution 70 contains a larger concentration of ions or to decrease the voltage if the influent solution **70** contains a smaller concentration of ions.

15   When the influent ion composition or concentrations are known and predictable over time, the controller **53** can also be preset to issue control signals that instruct the voltage supply **50** to pass predefined selected time average voltages during an ion removal or rejection step of the cell **22**. In this example, the controller **53** is preprogrammed with knowledge of the application, namely, the composition of the

20   influent solution **70** and/or the behavior of cell **22** over time or with the input volume of the influent solution **70**. The ion sensor **59** and feedback loop are absent. Controller **53** instructs variable supply **50** to adjust the voltage to cell **22** as a function of time or volume without an ion sensor **59** or closed loop control to sense a change in the ion concentration of the influent or effluent solutions **70, 80**.

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               In yet another version, the electrical resistance of cell **22** is used to determine or predict the conductivity of the effluent solution **80**, as shown in Figure 9, to control TDS in the effluent without controlling specific ion concentrations. In this version, the apparatus **20** comprises a voltmeter **62** to measure the voltage bias in the

30   cell **22** and generate a voltage signal and an ammeter **60** to measure the current in the cell **22** and generate a current signal. The controller **53** receives a voltage signal from the voltmeter **62** and the current signal from the ammeter **60** and calculates an ion concentration in the solution from the ratio of the voltage and current signals. The ratio of current/voltage represents the electrical resistance of the cell **22** and is an indicator

35   of the conductivity of the solution in the cell **22**, and thus a predictor of the effluent solution conductivity. Feedback loops **57** from the ammeter **60** and voltmeter **62**

provide the signals to controller **53** to allow the controller **53** to adjust the applied voltage to the cell **22** to maintain the ion concentration at a desired level. The measured cell resistance is a sum of water and membrane resistances, and thus controller **53** can also interpret the signals from feedback loops **57** to account for

5   changes in the membrane electrical resistance over time. In operation, the current/voltage ratio measurement is used to estimate ion concentration, and the controller **53** sends a control signal to the variable voltage supply **50** to adjust voltage in response to the measured current/voltage ratio.

10   Instead of a single cell **22**, the apparatus **20** can also comprise a plurality of cells **22** with solution inlets **30** and outlets **35** fluidly connected in a parallel or series arrangement. For example, an arrangement comprising two cells **22a,b** that have their influent inlets **30a,b** connected in parallel is shown in Figure 10a. In this arrangement, the influent water stream is split into two streams each of which provided to an influent

15   inlet **30a,b** of a separate cell **22a,b**. The effluent solution exits at each of the cell's outlets **35a,b** and is recombined prior to passing through or past an ion sensor **59**. The voltage supply **50** powers both cells **22a,b** in parallel. The signal from ion sensor **59** is carried to controller **53** by feedback loop **57** and the variable voltage supply **50** is adjusted accordingly in response to instructions in a control signal from the controller

20   **53**. This version is useful for operation at lower pressures or higher flow rates.

In yet another arrangement, two or more cells **22** are fluidly connected in series, with the influent solution entering a first cell **22a** at inlet **30a**, exiting the first cell's outlet **35a**, entering the inlet **30b** of a second cell **22b**, exiting at the second cell's

25   outlet **35b**, and finally passes past the ion sensor **59**, as shown in Figure 10b. The electrodes **40a,b, 45a,b** of both cells **22a,b** can be connected in parallel to a single voltage supply **50**, or each cell can have a separate voltage supply **50**. The controller **53** receives a signal from an ion sensor **59** relating to the ion content of the sequentially treated solution and controls the voltages applied to the electrodes **40a,b, 45a,b** in

30   each cell **22a,b** to control ion removal in each cell **22a,b**. In the version shown in Figure 10c, the first cell **22a** is power by a constant voltage supply **50c** that provides a single constant voltage to the cell **22a**, and the second cell **22b** is powered by a variable voltage supply **50**. The ion sensor **59** is located in the treated effluent solution **80** outside outlet **35b** of the second cell **22b**. In this embodiment, cell **22a** provides

35   maximum deionization as a pretreatment for the influent solution of the second cell **22b**, where the ion content of the cell is controlled to achieve desired ion levels. Ion sensor

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59, feedback loop 57, controller 53, and variable voltage supply 50 allow adjustment only of the voltage to cell 22b and not cell 22a.

EXAMPLE 1: Constant Voltage

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This example demonstrates the loss in ion removal efficiency of a water splitting ion exchange membrane 100 over an ion removal cycle. A cell 22 comprising a spiral wound water-splitting membrane 100 in a cylindrical housing 25 was employed for a TDS content reduction experiment. A constant voltage power supply with a

10   current limit of 1 A was used so a feedback circuit was not employed. The cell 22 comprised 30 layers of membrane 100 between a central electrode and an outer electrode. The cation exchange layer 51 of the membrane 100 faced outward and the anion exchange layer 49 inward. Initially, the cell 22 was regenerated by an ion rejection step for 20 minutes at 160 ml/min and 300 V using a feed water stream of ~50

15   μS/cm to prepare it for the deionization or ion removal step. During the regeneration step, the current to the electrodes 40, 45 was maintained at 0.5 to 1.0 amps, and the influent solution 70 was flowed from the inside to the outside of the spiral membrane 100 in the cell 22.

20   Subsequently, in a deionization or ion removal step, the influent solution flow direction and polarities of the time averaged voltage applied to the electrodes 40, 45 of the cell 22 were reversed. Influent solution 70 comprising water with dissolved solids or ions and having an initial ionic conductivity of 504 μS/cm was pumped through the cell 22 at 1.5 liters/minute. The voltage applied to the electrodes 40, 45 was the

25   maximum voltage available from the variable voltage power supply 50, namely, 300 V limited to 1 Amp maximum current. The result is shown in the graph of Figure 11, as the constant voltage curve in which full power was applied throughout the ion exchange cycle. The early high conductivity is due to purging the last regenerant solution from the cell 22 for the first 30 seconds, followed by a fairly stable conductivity output for 4

30   minutes, then a steady increase in effluent water conductivity occurred to 250 μS/cm at 16 minutes, when the experiment was stopped. This example demonstrates that the ion content in the effluent solution 80 gradually increased over time as the water splitting membrane 100 became saturated with ions removed from the influent solution 70. Consequently, the ionic concentration of the effluent solution 80 did not remain

35   constant during the treatment cycle, but instead varied by a factor of 5 corresponding to an increase in conductivity from 150 to 250 μS/cm.

EXAMPLE 2: Variable voltage

In this example, the apparatus **20** comprised the cell **22** of Example 1 having an ion sensor **59** that was a conductivity sensor that was connected to a controller **53** comprising a microprocessor to interpret the ion concentration signal and control the output voltage of a variable voltage supply **50**. The target ionic conductivity in this experiment was 125 μS/cm. Previous experiments determined the output voltages, which would be employed for various deviations of the ionic conductivity of the effluent solution **80** from the target conductivity. The result is presented in Figure 11 as the variable voltage curve. When the measured conductivity exceeded the 125 μS/cm target, the controller **53** increased the voltage to the cell **22**, and the conductivity of the effluent **80** was reduced soon thereafter. The slow variation up and down for the effluent solution **80** is a result of the finite response time of the system. This is largely dependent on the flow rate and void volume of the cell **22**. It is evident that the effluent solution conductivity is controlled in this illustration to 125 $\pm$ 25 μS/cm for a full 16 minutes, or 24 liters of treated solution. In contrast, the full (or single) power experiment in Example 1 provided treated effluent solution **80** in this target range for only 3 minutes, or for only 4.5 liters of volume.

The present apparatus **20** and methods allow treatment of influent solutions **70** to provide a selected or controlled ion concentration in the effluent solution **80**. For example, they can provide a treated effluent solution **80** comprising water having controlled concentration of ions most suitable for a particular purpose, whether it be taste for drinking water, hardness for softened water, or a particular TDS content for an industrial process. The present invention can also extend the working capacity of the deionization cycles of electrolytic ion exchange devices by avoiding the over-deionization of water, thereby preserving ion exchange capacity for further water treatment. By employing variable voltages rather than chemical systems, the complexity of the apparatus **20** is reduced, as is the capital and operating cost. Furthermore, the influent and effluent solutions avoid the risk of cross-contamination, which can occur when bleeding solutions to control ion concentrations. The apparatus **20** also provides good ion selectivity, resistance to mineral scale fouling, and concentrated regenerant effluent solutions typical of conventional ion exchange.

The present invention has been described in considerable detail with reference to exemplary versions thereof, however, other versions are possible, as

would be apparent to one of ordinary skill in the art. For example, other arrangements of electrochemical cells can also be used depending on the influent ion concentration, volume, or treatment desired. Also, alternative voltage supplies can be designed to provide voltages suitable for other applications, for example, a single polarity voltage having an AC component. Further, relative terms, such as first, second, outer, inner are provided only to illustrate the invention and are interchangeable with one another, for example, the first electrode can be the second electrode. Therefore the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.